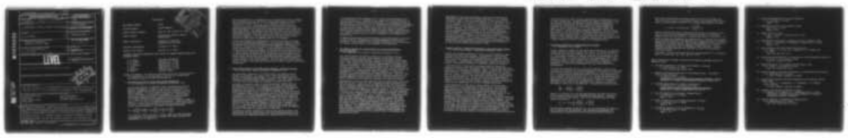
AD-A070 352 ROCHESTER UNIV N Y F/G 22/2
EXPERIMENTAL STUDIES OF VALENCE INSTABILITIES.(U)
JUN 79 R D PARKS DAAG29-76-G-0171
UNCLASSIFIED ARO-13428.1-P NL

1 OF 1
AD
A070352



END
DATE
FILMED
7-79
DDC

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ADA070352

DDC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 19 13428.1-P 18 ARO	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) 6 Experimental Studies of Valence Instabilities.		5. TYPE OF REPORT & PERIOD COVERED Final Report, 22 Mar 76 - 21 Mar 79
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 R. D. Parks		8. CONTRACT OR GRANT NUMBER(s) 15 DAAG29-76-G-0171
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Rochester, Rochester, New York 14627		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 8p.
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office, P. O. Box 12211, Research Triangle Park, NC 27709		12. REPORT DATE 11 Jun 79
		13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) LEVEL		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DDC JUN 22 1979 C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

valence instabilities
cerium metal
kondo lattice systems
cerium alloy
cerium intermetallics
rare earth systems
rare earth metal additives

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research accomplished is summarized in abstracts of five Ph.D. theses which were completed during the period: (1)"Experimental Studies of the $Ce_{(1-x)}Th_{(x)}$ Valence Instability,"(2) "Experimental Studies of Two Kondo Lattice Systems: $CeAl_{(2)}$ and $Ce_{(1-x)}Th_{(x)}$," (3)"Calorimetric Studies of a Cerium Alloy and a Cerium Intermetallic: $Ce_{(1-x)}Th_{(x)}$ and $CeAl_{(2)}$," (4) "Transport Studies of Cooperative Phenomena in Rare Earth Based Systems," and (5) "The Valence Instability in Cerium-Based Alloy Systems."

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

307 200 JOB

79 06 22 005

FINAL REPORT

ARO PROPOSAL NUMBER: 13428P

ARO GRANT NUMBER: DAA629-76-G-0171

PERIOD COVERED BY REPORT: March 22, 1976 to March 21, 1979

TITLE OF GRANT: Experimental Studies of Valence Instabilities

NAME OF INSTITUTION: University of Rochester
Rochester, New York 14627

PRINCIPAL INVESTIGATOR: Professor R. D. Parks

AUTHOR OF THIS REPORT: Professor R. D. Parks

SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

R. D. Parks	Principal Investigator
J. M. Lawrence	Received Ph.D. in 1976
M. C. Croft	Received Ph.D. in 1977
J. M. Markovics	Received Ph.D. in 1977
I. Zoric	Received Ph.D. in 1977
M. Manheimer	Received Ph.D. in 1978
B. Grier	Graduate Student

SUMMARY OF RESEARCH: The research accomplished during this reporting period is summarized below in the abstracts of the five Ph.D. theses which were completed during the same reporting period.

1. Experimental Studies of the $Ce_{1-x}Th_x$ Valence Instability
   J. M. Lawrence, Ph.D. Thesis, University of Rochester, 1976.

Cerium metal exhibits an isomorphic valence transition from the low density, paramagnetic, trivalent γ-state to the high density, non-magnetic, intermediate valence α-state without any change in the fcc lattice symmetry. In the x-T plane of the alloy system $Ce_{1-x}Th_x$ the line of first-order α-γ transitions terminates at a critical point. Utilizing electrical resistivity, which we show to couple linearly to the order parameter, we have located this critical point ($x_o = 0.265$, $T_o = 148$ K) and measured the critical exponent δ, whose value, $\delta = 3.0$ is that of a mean-field transition. A mean-field equation of state is found to fit the data in the critical region; and we obtain values for the parameters in the Landau free energy functional

$$\Delta F = s\left[\frac{A}{4}\left(\frac{\Delta n_f}{n_{fo}}\right)^4 + \frac{1}{2}\left(B\frac{\Delta x}{x_o} - C\Delta T\right)\left(\frac{\Delta n_f}{n_{fo}}\right)^2 + \left(D\frac{\Delta x}{x_o} - \Delta T\right)\left(\frac{\Delta n_f}{n_{fo}}\right)\right] .$$

$A = 118$ K, $B = 118$ K, $C = 0.35$, $D = 13$ K. Here n_f is the microscopic order parameter; the parameter s, obtained from recent specific heat measurements, is of order 0.4 R.

Mean field behavior is a consequence of long ranged forces, and is expected for the valence transition due to the strong electro-elastic coupling. We obtain lower limits on the $x = 0$ ($T = 0$) coherence length $\xi(x = 0) \gtrsim 7$ Å ($\xi(T = 0) \gtrsim 2$ Å). We discuss recent theories of the interaction responsible for the valence transition; and we argue that for an interaction propagated by the lattice the force range cannot be much larger than these lower limits. We attempt to show that the nature of the interaction, which appears as the $\Delta x \Delta n_f^2$ term in the free energy, is very much an open theoretical question. The other terms in the free energy are discussed; we show that in addition to the lattice coupling, the spin entropy of the cerium 4f electron plays an important role in the transition.

We have also measured the susceptibility $\chi(x,T)$ for a series of $Ce_{1-x}Th_x$ alloys with concentration embracing x_o. In the integral valence γ-state the susceptibility exhibits Curie-Weiss-like temperature dependence $\chi(x,T) = C/[T+\theta(x)]$. We argue that the origin of this behavior is an incipient valence fluctuation in the γ-state. In the intermediate valence α-state χ is essentially constant and enhanced, exhibiting only a weak variation with x. We use recent theoretical results to discuss 4f energy widths and their variation through the transition; we discuss also the relationship of the cerium valence instability to the Anderson-Kondo magnetic impurity problem. In the vicinity of the critical point we find that the effective moment χT couples linearly to the order parameter. We argue that this linear coupling (as well as that of the electrical resistivity ρ) stands in need of theoretical justification.

2. Experimental Studies of Two Kondo Lattice Systems: $CeAl_2$ and $Ce_{1-x}Th_x$.
M. C. Croft, Ph.D. Thesis, University of Rochester, 1977.

The experimental properties of two Kondo lattice (or Anderson lattice) systems are discussed. One system, $CeAl_2$ (often characterized in the past as a concentrated Kondo system), is in the local moment regime and undergoes an antiferromagnetic phase transition. The other system $Ce_{1-x}Th_x$ is in the mixed valent regime and undergoes a valence transition.

We present an extensive study of the polycrystalline thermal expansion and magnetostriction of $CeAl_2$ in fields up to 115KOe and temperatures below 20°K which reveals: 1) unambiguous verification of the previously disputed ordered nature of the low temperature phase (LTP) via the observation of domain effects in the LTP, 2) the phase diagram of the LTP, 3) the apparent presence upon increasing field of a continuous microscopic reorientation of the antiferromagnetic (AF) polarization to a direction transverse to the external field, 4) the presence of a small volume and large tetragonal magnetoelastic coupling in low field at T = 4.2K in the paramagnetic phase, 5) the presence of a distortion in the AF phase, 6) a value for the order parameter exponent in the AF phase of between .32 and .35, 7) the presence in high field of effects due to the mixing of the Γ_8 excited C.E.F. level with the Γ_7 ground state, and 8) the apparent presence of ferromagnetic interactions in high field.

Regarding the valence instability in the $Ce_{1-x}Th_x$ system we find 1) the phase diagram and the critical point for the γ-α phase transition in the concentration and temperature plane via a detailed study of resistivity,

2) the meanfield critical exponent of $\delta = 3$ from volume measurements near the critical point, 3) a coupling of the resistivity to the volume which to leading order is linear near the critical point, 4) an equation of state for the resistivity which accounts for the concentration and temperature dependence of the resistivity over a region of $T_c \pm 15°K$ and $.22<x<.41$, 5) an equation of state for the volume of the $Ce_{1-x}Th_x$ alloy which gives satisfactory semiquantitative predictions over almost the entire range of concentrations $0<x<1$, and for $300°K<T<0°$, and 6) that the essence of this equation of state is a Landau meanfield theory for the γ-α transition of Ce combined with Vegard's law.

An appendix generalizing the Weiss molecular field approximation numerically to high fields for ferromagnetic and antiferromagnetic interactions is presented. Another appendix with a general formulation of the Landau theory of a simple critical point in alloy systems is also presented.

3. Calorimetric Studies of a Cerium Alloy and a Cerium Intermetallic: $Ce_{1-x}Th_x$ and $CeAl_2$.
J. M. Markovics, Ph.D. Thesis, University of Rochester, 1977.

This thesis presents calorimetric studies of the archetypal valence transition material $Ce_{1-x}Th_x$, (whose behavior is equivalent to that of elemental Cerium under pressure), and the related Kondo lattice system $CeAl_2$. Face centered cubic $Ce_{1-x}Th_x$ undergoes an isomorphic phase transition in which volume is the macroscopic order parameter, (analogous to the liquid-gas transition), from a high temperature, high volume paramagnetic, integral valent phase, to a non-magnetic mixed valent, low volume state at low temperatures. $CeAl_2$, with the cubic $MgCu_2$ Laves structure, retains its paramagnetism to low temperatures, where it undergoes a cooperative transition to an exotic magnetically ordered ground state. Both $CeAl_2$ and the high temperature phase of $Ce_{1-x}Th_x$ display Kondo-like properties, and provide examples of a Kondo lattice, (that is a periodic array of local moments interacting with conduction electrons via a negative exchange).

Measurements on the Ce-Th alloy near the critical concentration showed that most, but not all, of the $R\,\ell n\,(2J+1)$ magnetic entropy is removed in the valence transition, demonstrating the quenching of the Ce^{3+} $J=5/2$ moment. Over a 200 degree interval, 1.42 R or $\sim$ 80% of the total spin entropy is removed; the remainder appears as electronic entropy. In the critical region $|T-T_o|/T_o \equiv |t| < 0.1$, the entropy couples linearly to the order parameter. A critical point analysis yields a strong symmetric divergence (prefactors $A = A'$) with the ϵ exponent $1 - 1/\delta$, $\delta = 2.85 \pm 0.24 \simeq 3$ indicating a mean field critical behavior of the valence transition. The entropy change under the peak calibrates the Landau free energy expression developed from resistivity and volumetric studies (see reference 19) and predicts the slope of the first order phase boundary at the critical point to be 23.7°K/kbar, which is approximately that observed for elemental Cerium under pressure. Low temperature measurements on the mixed valence ground state indicate a significant electronic effective mass enhancement, and intrinsic magnetic impurity effects. High magnetic fields increase the linear specific heat term over its zero field value, an unexplained and apparently new effect.

Measurements on the $CeAl_2$ intermetallic combined with dialatometric measurements established the low temperature phase (L.T.P.) diagram in magnetic field. A critical point analysis of the transition into the L.T.P. yields for the ratio of prefactor $A/A' = 0.62$ (+0.16, -0.13), and the exponent $\alpha = 0.008 \pm 0.04$, consistent with theoretical predictions for the single component 3-D Ising model, suggesting uniaxial magnetic ordering. The entropy change through the transition is 0.97 $R \ln 2$, corresponding to the removal of the Γ_7 doublet degeneracy. Antiferromagnetic order is confirmed by the observed negative magnetocaloric effect. Measurements on the pseudobinary intermetallic $Ce_{1-x}Pr_xAl_2$ indicates a possible spin glass regime below the magnetic ordering temperature as the Ce lattice is replaced by Pr. High field measurements on $CeAl_2$ indicate the predominance of ferromagnetic interactions above the ordered phase, leaving unresolved the mechanism of the exotic antiferromagnetism observed in $CeAl_2$.

4. Transport Studies of Cooperative Phenomena in Rare Earth Based Systems
I. L. Zoric, Ph.D. Thesis, University of Rochester, 1977.

We have used transport properties to study critical phenomena in three different rare earth based systems. The advantage of this approach compared to the use of an outside perturbation (i.e. neutrons, x-rays etc.) is that the system's own conduction electrons probe the critical fluctuations. A disadvantage of this approach is that the results are usually a complicated convolution of different correlation functions.

In the first part of the thesis we analyze electrical resistivity, thermoelectric power (TEP) and Lorentz number near the second order phase transition in the metallic ferromagnet $GdNi_2$. We think that the existing model based on a thermodynamic approach cannot account for the critical behavior of TEP. An extension of the Fisher-Langer model for resistivity near the critical point is constructed which accounts for the TEP behavior near the phase transitions. We have also carried out measurements of thermal conductivity κ near the critical point and although we observe an anomaly in κ, the Lorentz number shows no anomaly near the critical point, indicating the unimportance of inelastic scattering processes.

In the second part of this work we report studies on the rare earth compound $CeAl_2$ at low temperatures in magnetic field. The purpose of these studies is to shed some light on the transition from the high temperature crystal electric field modified Kondo behavior into the unknown ground state. We have determined that the phase diagram in the H-T plane consists of a single low temperature, low field region bounded by a smooth line of second order transitions. We have studied some thermodynamic and transport properties across the phase boundary. Although all the available thermodynamic quantities show critical behavior upon crossing the phase boundary we observe no critical anomaly in electrical resistivity. The nature of the ground state of $CeAl_2$ is discussed in terms of the competition between the formation of a magnetically ordered state due to the RKKY coupling and the tendency to form Kondo singlets. We also indicate how one possible structure of the order parameter can lead to the absence of a critical anomaly in the derivative of electrical resistivity.

The last part of the thesis concerns another type of critical point, i.e., a valence instability. We report studies of transport coefficients in the $Ce_{1-x}Th_x$ and the CeThLa systems which exhibit valence instabilities. In the integral valence phase the TEP is large and strongly temperature dependent with a sharp cut off occurring at the valence instability. Below the valence instability, i.e., in the mixed valence phase, the TEP is small (+ 7-8μV) and weakly temperature dependent. We will discuss the behavior of the TEP in both the integral valence and the mixed valence phase in terms of current models. These models are extensions of the Anderson single impurity model to the concentrated case with allowances for coupling to the different kinds of bosons (electron-hole excitations of the d band or phonons) as well as in terms of the paramagnon model.

5. The Valence Instability in Cerium-Based Alloy Systems
M. A. Manheimer, Ph.D. Thesis

We have studied the effects of rare earth metal additives on the isomorphic valence transition of face-centered cubic cerium. The alloys studied are of the form $Ce_{0.9-x}RE_xTh_{0.1}$ with RE = Sc, Th, La, Eu, Gd, Dy, Er, Yb, and Lu. The thorium is present to suppress formation of the hexagonal β phase cerium allotrope. The transition from the high temperature, high volume, parametric γ phase to the low temperature, collapsed, nonmagnetic α phase is characterized by a large change ($\sim$ 90 $\mu\Omega$-cm) in spin scattering resistivity, so resistivity measurements have been used throughout the investigation.

The alloy phase diagrams in the T-x plane are analogous to those in the T-P plane (P = pressure) for liquid-gas systems in that there is a coexistence curve separating the two phases which terminates in a critical point (T_o,x_o). For $x < x_o$ the resistive transitions exhibit typical first order behavior, while continuous transitions occur for $x > x_o$. We have determined the alloy phase diagrams, and have found for each of the systems that the transition temperature varies linearly with concentration. There is a systematic dependence of the slope of the coexistence curve (dT_c/dx) on valence (N) and metallic radius (R) of the additives. The observed functional form is:

$$\frac{dT_c}{dx} = -70\left(\frac{R-R_o}{R_o}\right) + 30\left(\frac{N-N_o}{N_o}\right)$$

where $R_o = 1.759$ and $N_o = 3.66$ are identified with the values for cerium at the critical point, and x is measured in atomic percent. Ytterbium acts 2.2 valent in this system. The critical concentrations are found to obey the relation:

$$x_o = 15 + 0.625\left\{-75\left(\frac{R-R_o}{R_o}\right) + 28\,\frac{N-N_o}{N_o}\right\}$$

The correlation between dT_c/dx and x_o is not well understood and stands in need of theoretical justification. The interactions responsible for renormalizing T_c apparently also drive the system towards criticality.

Mean field critical behavior has been observed for the four systems with RE = Th, La, Gd, and Yb. The resistivity data in the region of the critical points of these systems has been fit to a Landau theory equation of state:

$$T = a(\Delta V)^3 + b'(\Delta V)(\Delta R)(\Delta x) + \left(\frac{T_o - 140}{T_o}\right)\Delta x$$

where ΔV measures the value of the resistivity scaled to the critical value, and ΔT, ΔR, Δx are the corresponding scaled quantities for temperature, metallic radius and concentration. We obtain the values $a = 0.52$ and $b' = 22$.

While the term which determines the depression of T_c, $[(T_o-140)/T_o]\Delta x$ depends both on size and valence of the additive, the interaction term $b'(\Delta V)(\Delta R)(\Delta x)$ depends only on solute size ΔR. This strongly suggests that while electronic and lattice effects are equally important in determining T_c, a lattice mechanism is responsible for the cooperative phase transition. Possible transition driving mechanisms are discussed in light of the prevailing theoretical models.

Note added: Corrections to above numerical results appear in M. A. Manheimer and R. D. Parks, Phys. Rev. Lett. 42, 321 (1979).

LIST OF PUBLICATIONS (REFEREED) RESULTING FROM RESEARCH PERFORMED DURING THIS REPORTING PERIOD:

1. The Valence Instability and Associated Phenomena in $Ce_{1-x}Th_x$
   J. M. Lawrence and R. D. Parks
   J. Phys. (France) 37, C4-249 (1976)

2. Magnetic and Electric Properties of Cerium-Based Alloys: The Effects of the Valence Transiton
   J. M. Lawrence and R. D. Parks
   Proceedings of the Twelfth Rare Earth Research Conference, Part II, edited by C. E. Lundin (Denver Research Institute, 1976) p. 977.

3. Thermodynamical Behavior at Valence Instabilities
   J. M. Lawrence, M. C. Croft and R. D. Parks
   Valence Instabilities and Related Narrow Band Phenomena, edited by R. D. Parks (Plenum Press, 1977) p. 35.

4. Spin Susceptibility of Chemically Collapsed Cerium
   J. M. Lawrence and R. D. Parks
   ibid, p. 443.

5. Effect of Additives on the Valence Transition of Cerium
   M. A. Manheimer and R. D. Parks
   ibid, p. 447.

6. Calorimetric Studies of the γ-α Transition in $Ce_{1-x}Th_x$
   J. M. Markovics and R. D. Parks
   ibid, p. 451.

7. Elastic Measurements Near a Valence Transition
M. C. Croft and R. D. Parks
ibid, p. 455.

8. Thermoelectric Power of Cerium-Based Systems
I. Zoric and R. D. Parks
ibid, p. 459.

9. Wither Goest Thou $CeAl_2$?
M. Croft, I. Zoric, J. Markovics and R. Parks
ibid, p. 475.

10. Thermodynamic and Transport Properties of $CeAl_2$ in Magnetic Field
I. Zoric, J. Markovics, L. Kupferberg, M. Croft and R. D. Parks
ibid, p. 479.

11. Spin Dynamics in the Mixed Valence Alloy $Ce_{1-x}Th_x$
S. M. Shapiro, J. D. Axe, R. J. Birgeneau, J. M. Lawrence and R. D. Parks
Phys. Rev. 16, 2225 (1977).

12. Anisotropic Magnetostriction in $CeAl_2$ Near Its Antiferromagnetic Transition
M. C. Croft, I. Zoric and R. D. Parks
Phys. Rev. B 18, 345 (1978).

13. Thermal Expansion in the Anderson Lattice System, $CeAl_2$
M. C. Croft, I. Zoric and R. D. Parks
Phys. Rev. B 18, 5065 (1978).

14. Scaling Studies of the Valence Transition in Cerium-Based Solid Solutions
M. A. Manheimer and R. D. Parks
J. Phys. (France) (accepted, in press).

15. Ground State Properties and Energy Parameters of the Anderson Lattice System, $CeAl_2$
R. D. Parks, L. C. Kupferberg, M. A. Manheimer, S. M. Shapiro and E. Gurewitz
J. Phys. (France) (accepted, in press).

16. Evidence of a Multiple q Structure in $CeAl_2$
E. Gurewitz, S. M. Shapiro, L. C. Kupferberg and R. D. Parks
Proceedings of Twenty-Fourth Annual Conference on Magnetism and Magnetic Materials (accepted).

17. Valence Transition in Chemically Collapsed Cerium
M. A. Manheimer and R. D. Parks
Phys. Rev. Letters 42, 321 (1979).